DESCRIPTION

GALVANIZED STEEL SHEET EXCELLENT IN POST-PAINTING CORROSION RESISTANCE AND PAINT COAT IMAGE CLARITY

Technical Field

The present invention relates to a plated steel sheet and, more specifically, to a plated steel sheet having excellent post-plating corrosion resistance and post-plating brightness and applicable to various applications such as home electric appliances, automobiles and building materials.

Background Art

Among plated steel sheets most commonly recognized as having a good corrosion resistance, there are galvanized-type steel sheets. Such galvanized-type steel sheets are used in various manufacturing industries including the fields of automobiles, home electric appliances and building materials and most of them are used, after being painted, from the viewpoint of corrosion resistance and designability.

The present inventors, with the aim of improving the corrosion resistance of such galvanized-type steel sheets, have proposed Zn-Al-Mg-Si hot dip plated steel sheets in Japanese Patent No. 3179446. Further, the present inventors have clarified, in Japanese Unexamined Patent Publication No. 2000-064061, the fact that a painted steel sheet more excellent in corrosion resistance can be obtained by adding one or more elements of Ca, Be, Ti, Cu, Ni, Co, Cr and Mn to such a proposed Zn-Al-Mg-Si hot dip plated steel sheet.

Furthermore, Japanese Unexamined Patent Publication No. 2001-295015 describes the fact that a surface appearance is improved by adding Ti, B and Si to a Zn-Al-Mg hot dip plated steel sheet.

However, with the aforementioned prior arts and

other disclosed plated steel sheets, sufficient corrosion resistance and paint coat image clarity are not always secured in the case where they are used after being processed and painted.

Disclosure of the Invention

The object of the present invention is to provide a plated steel sheet excellent in post-painting corrosion resistance and paint coat image clarity by solving the aforementioned problems. The present inventors, as a result of earnestly repeating research on the development of a plated steel sheet excellent in post-painting corrosion resistance and paint coat image clarity, have arrived at the present invention by finding: that the paint coat image clarity improves by controlling the center line average roughness Ra of a steel sheet, which has a galvanized layer containing Mg of 1 to 10%, Al of 2 to 19% and Si of 0.001 to 2% in mass, to 1.0 μm or less and the filtered waviness curve W_{CA} thereof to 0.8 μm or less; and further that the post-painting corrosion resistance further improves by adding one or more elements selected from among Ca, Be, Ti, Cu, Ni, Co, Cr and Mn into the galvanized layer and optimizing the addition amounts. That is, the gist of the present invention is as follows;

(1) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image clarity, characterized in that the center line average roughness Ra of said steel sheet is 1.0 μm or less and the filtered waviness curve W_{CA} thereof is 0.8 μm or less, said steel sheet having on the surface thereof a galvanized layer containing 1 to 10% of Mg, 2 to 19% of Al and 0.001 to 2% of Si in mass with the balance consisting of Zn and unavoidable impurities.

(2) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image

clarity, characterized in that said plated layer of said galvanized steel sheet according to the item (1) further contains one or more elements selected from among Ca of 0.01 to 0.5%, Be of 0.01 to 0.2%, Ti of 0.0001 to 0.2%, Cu of 0.1 to 10%, Ni of 0.001 to 0.2%, Co of 0.01 to 0.3%, Cr of 0.0001 to 0.2% and Mn of 0.01 to 0.5% in mass.

(3) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image clarity according to the item (1) or (2), characterized in that said plated layer has a metallographic structure wherein an [Mg_2Si phase], a [Zn_2Mg phase] and a [Zn phase] coexist in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure].

(4) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image clarity according to the item (1) or (2), characterized in that said plated layer has a metallographic structure wherein an [Mg_2Si phase], a [Zn_2Mg phase] and an [Al phase] coexist in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure].

(5) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image clarity according to the item (1) or (2), characterized in that said plated layer has a metallographic structure wherein an [Mg_2Si phase], a [Zn_2Mg phase], a [Zn phase] and an [Al phase] coexist in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure].

(6) A galvanized steel sheet excellent in post-painting corrosion resistance and paint coat image clarity according to the item (1) or (2), characterized in that said plated layer has a metallographic structure wherein an [Mg_2Si phase], a [Zn phase] and an [Al phase] coexist in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure].

Best Mode for Carrying Out the Invention

The present invention is hereunder explained in detail.

A galvanized steel sheet according to the present invention is a galvanized steel sheet characterized in that the center line average roughness Ra (JIS B0601) of the galvanized steel sheet is 1.0 μm or less and the filtered waviness curve W_{CA} (JIS B0601) thereof is 0.8 μm or less, the galvanized steel sheet having a galvanized layer containing Mg of 1 to 10%, Al of 2 to 19% and Si of 0.001 to 2% in mass.

The reason for limiting the Mg content to 1 to 10% in mass is that, when the Mg content is less than 1% in mass, the effect of improving corrosion resistance is insufficient and, when it exceeds 10% in mass, the galvanized layer embrittles and the adhesiveness deteriorates.

The reason for limiting the Al content to 2 to 19% in mass is that, when the Al content is less than 2% in mass, the galvanized layer embrittles and the adhesiveness deteriorates and, when it exceeds 19% in mass, the effect of improving corrosion resistance disappears.

The reason for limiting the Si content to 0.001 to 2% in mass is that, when the Si content is less than 0.001% in mass, Al in the galvanized layer reacts with Fe in the steel sheet, the galvanized layer embrittles and the adhesiveness deteriorates and, when it exceeds 2% in mass, the effect of improving adhesiveness disappears.

The reason for limiting the Ra value to 1.0 μm or less is that, when it exceeds 1.0 μm, the paint coat image clarity deteriorates. The reason for limiting the W_{CA} value to 0.8 μm or less is that, when it exceeds 0.8 μm, the paint coat image clarity deteriorates. The lower limits of Ra and W_{CA} values are not particularly regulated because the paint coat image clarity improves

as the values of Ra and W_{CA} fall. However, it is substantially difficult to stably obtain Ra and W_{CA} values of 0.01 μm or less on an industrial scale.

In the present invention, a method for imposing roughness on a plated surface is not particularly limited and any method is acceptable as far as the expressions Ra ≤ 1.0 μm and W_{CA} ≤ 0.8 μm are secured. For example, skin-pass rolling or the like, wherein rolls adjusted to Ra ≤ 1.0 μm and W_{CA} ≤ 0.8 μm by applying laser dull machining or electrical discharge dull machining are used, can be employed.

In order to further improve post-painting corrosion resistance, one or more elements selected from among Ca, Be, Ti, Cu, Ni, Co, Cr and Mn are added. The reasons why the addition of those elements causes the post-painting corrosion resistance to improve are presumably that;

1. the fine jogs formed on the surface of a galvanized layer make the anchor effect on a painted film increase,

2. the addition of the elements makes fine micro-cells form in a galvanized layer and improves the reactivity and adhesiveness to a chemical conversion coating,

3. the addition of the elements stabilizes corrosion products in a galvanized layer and delays the corrosion of the galvanized layer under a painted film.

The effect of further improving post-painting corrosion resistance appears conspicuously when the contents of Ca, Be, Ti, Cu, Ni, Co, Cr and Mn are 0.01% or more, 0.01% or more, 0.0001% or more, 0.1% or more, 0.001% or more, 0.01% or more, 0.0001% or more and 0.01% or more in mass, respectively, and therefore the respective lower limits are set at those figures.

On the other hand, when the addition amounts increase, the surface appearance after plating becomes coarse and a poor appearance occurs due to the deposition

of, for example, dross or oxide and, therefore, the upper limits of the elements Ca, Be, Ti, Cu, Ni, Co, Cr and Mn are set at 0.5%, 0.2%, 0.2%, 1.0%, 0.2%, 0.3%, 0.2% and 0.5% in mass, respectively.

Further, the addition of one or more elements selected from among Ca, Be, Ti, Cu, Ni, Co, Cr and Mn is effective also for the fractionization of the crystals in a plated layer and therefore it is estimated that the addition of those elements lowers the surface roughness and contributes also to the improvement of paint coat image clarity.

Besides those elements, Fe, Sb, Pb and Sn may be contained individually or in combination by 0.5% or less in mass in a galvanized layer. Further, even when P, B, Nb, Bi and the third group elements are contained at 0.5% or less in mass in total, the effect of the present invention is not hindered and rather, in some favorable cases, formability is further improved depending on the addition amount.

In the present invention, in order to obtain a galvanized steel sheet further excellent in corrosion resistance, it is desirable to further increase the addition amounts of Si, Al and Mg and to form a metallographic structure wherein an [Mg_2Si phase] is mixed in the solidification structure of a galvanized layer. It becomes possible to further improve corrosion resistance by increasing the addition amounts of Al, Mg and Si and forming a metallographic structure wherein an [Mg_2Si phase] is mixed in the solidification structure of a plated layer. To that end, it is preferable to control an Mg content to 2% or more and an Al content to 4% or more in mass.

A plated layer according to the present invention is mainly composed of a quaternary alloy of Zn-Mg-Al-Si. In this case, when the amounts of Al and Mg are relatively small, the material shows a behavior similar to a binary alloy of Zn-Si in the early stages of solidification and

primary crystals of Si type crystallize. Thereafter, the material shows a solidification behavior similar to a ternary alloy of Zn-Mg-Al composed of the remainder. That is, after an [Si phase] crystallizes primarily, a metallographic structure containing one or more of a [Zn phase], an [Al phase] and a [Zn_2Mg phase] in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure] forms.

Then, when the amounts of Al and Mg increase to some extent, the material shows a behavior similar to a ternary alloy of Al-Mg-Si in the early stages of solidification and primary crystals of Mg_2Si type crystallize. Thereafter, the material shows a solidification behavior similar to a ternary alloy of Zn-Mg-Al composed of the remainder. That is, after an [Mg_2Si phase] crystallizes primarily, a metallographic structure containing one or more of a [Zn phase], an [Al phase] and a [Zn_2Mg phase] in the substrate of an [Al/Zn/Zn_2Mg ternary eutectic structure] forms.

Here, an [Si phase] is the phase that looks like an island having a clear boundary in the solidification structure of a plated layer, for example, the phase that corresponds to primary crystal Si in a Zn-Si binary phase equilibrium diagram. In some actual cases, a small amount of Al may dissolve in the phase and thus, as long as it is observed in the phase diagram, it is estimated that Zn and Mg do not dissolve or, even if they dissolve, their dissolved amounts are very small. In this case, the [Si phase] can be clearly identified in the plated layer under microscopic observation.

Further, an [Mg_2Si phase] is the phase that looks like an island having a clear boundary in the solidification structure of a plated layer, for example, the phase that corresponds to primary crystal Mg_2Si in an Al-Mg-Si ternary phase equilibrium diagram. As long as it is observed in the phase diagram, it is estimated that Zn and Al do not dissolve or, even if they dissolve,

their dissolved amounts are very small. In this case, the [Mg_2Si phase] can be clearly identified in the plated layer under microscopic observation.

Furthermore, an [Al/Zn/Zn_2Mg ternary eutectic structure] is the ternary eutectic structure comprising an [Al phase], a [Zn phase] and an [intermetallic compound Zn_2Mg phase]. The [Al phase] which composes the ternary eutectic structure corresponds to, for example, an [Al" phase] (an Al solid solution that contains Zn in the state of a solid solution and includes a small amount of Mg) at a high temperature in an Al-Zn-Mg ternary phase equilibrium diagram. An [Al" phase] at a high temperature usually appears in the state of separating into a fine Al phase and a fine Zn phase at an ordinary temperature. Further, the Zn phase in the ternary eutectic structure contains a small amount of Al in the state of a solid solution and, in some cases, is a Zn solid solution wherein a small amount of Mg is dissolved further. The Zn_2Mg phase in the ternary eutectic structure is an intermetallic compound phase existing in the vicinity of the point indicated at about 84% in mass of Zn in the Zn-Mg binary phase equilibrium diagram. As long as it is observed in the phase diagram, it is estimated that Si dissolves or does not in each phase or, even if it dissolves, the dissolved amount is very small. However, as the very small dissolved amount cannot be clearly identified with an ordinary analysis, the ternary eutectic structure composed of the three phases is expressed by the term [Al/Zn/Zn_2Mg ternary eutectic structure] in DESCRIPTION of the present invention.

Yet further, an [Al phase] is a phase that looks like an island having a clear boundary in the substrate of the aforementioned ternary eutectic structure and the phase corresponds to, for example, an [Al" phase] (an Al solid solution that contains Zn in the state of a solid solution and includes a small amount of Mg) at a high temperature in an Al-Zn-Mg ternary phase equilibrium

diagram. In an Al" phase at a high temperature, the amounts of dissolved Zn and Mg vary in accordance with the concentrations of Al and Mg in a plating bath. An Al" phase at a high temperature usually separates into a fine Al phase and a fine Zn phase at an ordinary temperature and it is reasonably estimated that the island shape observed at an ordinary temperature is the residue of the Al" phase at a high temperature. As long as it is observed in the phase diagram, it is estimated that Si dissolves or does not dissolve in the phase or, even if it dissolves, the dissolved amount is very small. However, as the very small dissolved amount cannot clearly be identified with an ordinary analysis, the phase that derives from the Al" phase (called Al primary crystals) at a high temperature and retains the shape of the Al" phase is called an [Al phase] in DESCRIPTION of the present invention. In this case, the [Al phase] can clearly be distinguished from the Al phase composing the aforementioned ternary eutectic structure under microscopic observation.

Yet further, a [Zn phase] is the phase that looks like an island having a clear boundary in the substrate of the aforementioned ternary eutectic structure and, in some actual cases, a small amount of Al and, further, a small amount of Mg, may dissolve in the phase. As long as it is observed in the phase diagram, it is estimated that Si does not dissolve in the phase or, even if it dissolves, the dissolved amount is very small. In this case, the [Zn phase] can clearly be distinguished from the Zn phase composing the aforementioned ternary eutectic structure under microscopic observation.

Yet further, a [Zn_2Mg phase] is the phase that looks like an island having a clear boundary in the substrate of the aforementioned ternary eutectic structure and, in some actual cases, a small amount of Al may dissolve in the phase. As long as it is observed in the phase diagram, it is estimated that Si does not dissolve in the

phase or, even if it dissolves, the dissolved amount is very small. In this case, the [Zn_2Mg phase] can clearly be distinguished from the Zn_2Mg phase composing the aforementioned ternary eutectic structure under microscopic observation.

In the present invention, though the crystallization of an [Si phase] does not particularly influence the improvement of corrosion resistance, the crystallization of a [primary crystal Mg_2Si phase] obviously contributes to the improvement of corrosion resistance. The contribution is presumably caused by the facts that Mg_2Si is very active and that Mg_2Si reacts with water and is decomposed in a corrosive environment, protects a metallographic structure, wherein one or more of a [Zn phase], an [Al phase] and a [Zn_2Mg phase] are contained in the substrate of an [$Al/Zn/Zn_2Mg$ ternary eutectic structure], from corrosion in a sacrificial manner, simultaneously forms a protective film by the produced Mg hydroxide, and suppresses further progress of corrosion.

Further, it is estimated that, when one or more elements of Ca, Be, Ti, Cu, Ni, Co, Cr and Mn are added to a Zn-Mg-Al-Si quaternary alloy, some of the elements dissolve and some other elements form intermetallic compounds by combining with Zn, Al, Mg and the added elements. However, with the addition amounts in the ranges stipulated in the present invention, it is difficult to clearly identify the shapes by an ordinary analysis method and for that reason their addition amounts are not particularly defined.

Though the deposition amount of plating is not particularly regulated, a desirable amount is 10 g/m^2 or more from the viewpoint of corrosion resistance and 350 g/m^2 or less from the viewpoint of workability.

In the present invention, a method for producing a plated steel sheet is not particularly regulated and an ordinary non-oxidizing furnace type hot dip plating method can be applied. In the case of applying Ni pre-

plating as a lower layer too, an ordinarily employed pre-plating method may be applied and a preferable method after the Ni pre-plating is to apply rapid low-temperature heating in a non-oxidizing or reducing atmosphere and thereafter to apply hot dip plating. The present invention is explained concretely on the basis of Examples.

Example 1

Firstly, cold-rolled steel sheets 0.8 mm in thickness were prepared, and subjected to hot dip plating for three seconds at 400 to 500°C in a Zn alloy plating bath wherein the amounts of added elements were changed, to N_2 wiping for adjusting the plated amount to 70 g/m^2, and to skin-pass rolling with rolls the roughness of which was changed. The chemical compositions of the plated layers and the surface roughness of the plated steel sheets thus produced are shown in Table 1.

The values of Ra and W_{CA} were measured under the following measurement conditions with a surface roughness shape measuring instrument (made by Tokyo Seimitsu Co., Ltd.). The roughness was measured at three arbitrary points and the average value was used.

Probe: probe tip 5 μmR

Measurement length: 25 mm

Cutoff: 0.8 mm

Driving speed: 0.3 mm/sec.

Filter: 2CR filter

The paint coat image clarity was evaluated by cutting a plated steel sheet to a size of 150 mm x 70 mm, subjecting the steel sheet to chemical conversion treatment and painting, and then using a mapping definition measuring instrument (made by Suga Test Instruments Co., Ltd.). A phosphate, at 2 g/m^2, was applied as the chemical conversion treatment and cathodic electrodeposition painting to 20 μm and polyester

intermediate and finish coats to 35 μm each were applied as the painting. The paint coat image clarity was evaluated by measuring the NSIC and scoring it in accordance with the following criterion. The mark 3 was judged to be acceptable.

3: 85 or more

2: 70 or more to less than 85

1: less than 70

The results of the evaluations are shown in Table 1.

In the cases of Nos. 3 to 5, 8, 11, 14, 17, 20, 23, 26 and 29, the surface roughness was outside the range stipulated in the present invention and therefore the paint coat image clarity was unacceptable. In all the other cases, good paint coat image clarity was obtained.

Table 1

No.	Hot dip galvanized layer composition (mass%)											Surface roughness		Brightness	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn	Ra	W_{CA}		
1	3	11	0.15									0.35	0.42	3	Invention
2	3	11	0.15									0.98	0.77	3	Invention
3	3	11	0.15									1.21	1.06	2	Comparative
4	3	11	0.15									1.10	0.73	2	Comparative
5	3	11	0.15									0.88	0.91	2	Comparative
6	3	11	0.15	0.05								0.55	0.49	3	Invention
7	3	11	0.15	0.05								0.95	0.78	3	Invention
8	3	11	0.15	0.05								1.32	1.13	2	Comparative
9	3	11	0.15		0.03							0.47	0.64	3	Invention
10	3	11	0.15		0.03							0.96	0.77	3	Invention
11	3	11	0.15		0.03							1.27	1.08	2	Comparative
12	3	11	0.15			0.03						0.39	0.45	3	Invention
13	3	11	0.15			0.03						0.92	0.76	3	Invention
14	3	11	0.15			0.03						1.40	1.12	2	Comparative
15	3	11	0.15				0.31					0.43	0.51	3	Invention
16	3	11	0.15				0.31					0.97	0.78	3	Invention
17	3	11	0.15				0.31					1.27	1.15	2	Comparative
18	3	11	0.15					0.03				0.57	0.63	3	Invention
19	3	11	0.15					0.03				0.96	0.78	3	Invention
20	3	11	0.15					0.03				1.27	1.09	2	Comparative
21	3	11	0.15						0.04			0.41	0.53	3	Invention
22	3	11	0.15						0.04			0.96	0.77	3	Invention
23	3	11	0.15						0.04			1.28	1.17	2	Comparative
24	3	11	0.15							0.03		0.52	0.46	3	Invention
25	3	11	0.15							0.03		0.97	0.78	3	Invention
26	3	11	0.15							0.03		1.33	1.15	2	Comparative
27	3	11	0.15								0.03	0.38	0.44	3	Invention
28	3	11	0.15								0.03	0.93	0.78	3	Invention
29	3	11	0.15								0.03	1.41	1.11	2	Comparative
30	4	8	0.25									0.38	0.43	3	Invention
31	5	10	0.3									0.45	0.57	3	Invention
32	6	4	0.12									0.52	0.61	3	Invention
33	5	15	1.5									0.64	0.49	3	Invention
34	1	2	0.06									0.76	0.52	3	Invention
35	3	19	0.5									0.81	0.60	3	Invention
36	3	6	0.005									0.39	0.42	3	Invention
37	3	11	0.15			0.0002						0.44	0.56	3	Invention
38	3	11	0.15					0.003				0.57	0.61	3	Invention
39	3	11	0.15							0.0003		0.51	0.48	3	Invention

Example 2

Firstly, cold-rolled steel sheets 0.8 mm in thickness were prepared, and subjected to hot dip plating for three seconds at 400 to 500°C in a Zn alloy plating bath wherein the amounts of added elements were changed, to N_2 wiping for adjusting the plated amount to 70 g/m^2, and to skin-pass rolling with rolls of small roughness so as to control the center line average roughness Ra and the filtered waviness curve W_{CA} of the plated steel sheets to 1.0 μm or less and 0.8 μm or less, respectively. The chemical compositions of the plated layers of the plated steel sheets thus produced are shown

in Tables 2 and 3.

The plated steel sheets thus produced were cut into the size of 200 mm x 200 mm, stretched by 35 mm by using a punch 100 mm in diameter with a spherical head, and thereafter subjected to chemical conversion treatment, painting and the evaluation of corrosion resistance. A phosphate, at 2 g/m^2, was applied as the chemical conversion treatment and the cathodic electrodeposition painting of 20 μm and polyester intermediate and finish coats to 35 μm each were applied as the painting.

Further, the painted steel sheets thus produced were scratched, to reached the substrate steel, with a utility knife and then subjected for 120 cycles to CCT comprising 4 hour SST, 2 hour drying and 2 hour humidifying as a sequential cycle. The evaluation was made by applying tape exfoliation test to the scratches after corrosion test and scoring in accordance with the following criterion based on the length of the exfoliation of a painted film. The marks 4 and 5 were judged to be acceptable.

5: less than 5 mm

4: 5 mm or more to less than 10 mm

3: 10 mm or more to less than 20 mm

2: 20 mm or more to less than 30 mm

1: 30 mm or more

The paint coat image clarity was evaluated by cutting a plated steel sheet into a size of 150 mm x 70 mm, subjecting the steel sheet to chemical conversion treatment and painting, and then using image distinctness measuring instrument (made by Suga Test Instruments Co., Ltd.). A phosphate, to 2 g/m^2, was applied as the chemical conversion treatment and the cathodic electrodeposition painting of 20 μm and polyester intermediate and finish coats to 35 μm each were applied as the painting. The paint coat image clarity was evaluated by measuring the NSIC and scoring it in

accordance with the following criterion. The mark 3 was judged to be acceptable.

3: 85 or more

2: 70 or more to less than 85

1: less than 70

The results of the evaluations are shown in Tables 2 and 3.

In the cases of Nos. 56 and 60, the contents of Ca, Be, Ti, Cu, Ni, Co, Cr and Mn in the plated layers were outside the ranges stipulated in the present invention and, as a result, the post-painting corrosion resistance was unacceptable. In the case of No. 57, the contents of Mg, Al, Si, Ca, Be, Ti, Cu, Ni, Co, Cr and Mn in the plated layer were outside the ranges stipulated in the present invention and resultantly the post-painting corrosion resistance was unacceptable. In the case of No. 58, the content of Al in the plated layer was outside the range stipulated in the present invention and, as a result, the post-painting corrosion resistance was unacceptable. In the case of No. 59, the contents of Mg, Si, Ca, Be, Ti, Cu, Ni, Co, Cr and Mn in the plated layer were outside the ranges stipulated in the present invention and resultantly the post-painting corrosion resistance was unacceptable. In all the other cases, good post-painting corrosion resistance and brightness were obtained.

Table 2

No.	Hot dip galvanized layer composition (mass%)											Surface roughness		P-painting corrosion resistance	Brightness	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn	Ra	W_{CA}			
1	3	11	0.15	0.05								0.7	0.6	5	3	Invention
2	3	11	0.15		0.03							0.7	0.6	5	3	Invention
3	3	11	0.15			0.03						0.7	0.6	5	3	Invention
4	3	11	0.15			0.01						0.7	0.6	5	3	Invention
5	3	11	0.15			0.05						0.7	0.6	5	3	Invention
6	3	11	0.15				0.31					0.7	0.6	5	3	Invention
7	3	11	0.15					0.03				0.7	0.6	5	3	Invention
8	3	11	0.15					0.01				0.7	0.6	5	3	Invention
9	3	11	0.15					0.08				0.7	0.6	5	3	Invention
10	3	11	0.15						0.04			0.7	0.6	5	3	Invention
11	3	11	0.15						0.01			0.7	0.6	5	3	Invention
12	3	11	0.15						0.05			0.7	0.6	5	3	Invention
13	3	11	0.15							0.03		0.7	0.6	5	3	Invention
14	3	11	0.15							0.01		0.7	0.6	5	3	Invention
15	3	11	0.15								0.03	0.7	0.6	5	3	Invention
16	3	11	0.15								0.01	0.7	0.6	5	3	Invention
17	3	11	0.15								0.1	0.7	0.6	5	3	Invention
18	3	11	0.15	0.02	0.02							0.7	0.6	5	3	Invention
19	3	11	0.15	0.02		0.02						0.7	0.6	5	3	Invention
20	3	11	0.15	0.02			0.2					0.7	0.6	5	3	Invention
21	3	11	0.15	0.02				0.02				0.7	0.6	5	3	Invention
22	3	11	0.15	0.02					0.02			0.7	0.6	5	3	Invention
23	3	11	0.15	0.02						0.02		0.7	0.6	5	3	Invention
24	3	11	0.15	0.02							0.02	0.7	0.6	5	3	Invention
25	3	11	0.15		0.02	0.02						0.7	0.6	5	3	Invention
26	3	11	0.15		0.02		0.2					0.7	0.6	5	3	Invention
27	3	11	0.15		0.02			0.02				0.7	0.6	5	3	Invention
28	3	11	0.15		0.02				0.02			0.7	0.6	5	3	Invention
29	3	11	0.15		0.02					0.02		0.7	0.6	5	3	Invention
30	3	11	0.15		0.02						0.02	0.7	0.6	5	3	Invention
31	3	11	0.15			0.02	0.2					0.7	0.6	5	3	Invention
32	3	11	0.15			0.02		0.02				0.7	0.6	5	3	Invention
33	3	11	0.15			0.02			0.02			0.7	0.6	5	3	Invention

Table 3

No.	Hot dip galvanized layer composition (mass%)											Surface roughness		P-painting corrosion resistance	Brightness	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn	Ra	W_{CA}			
34	3	11	0.15			0.02				0.02		0.7	0.6	5	3	Invention
35	3	11	0.15			0.02					0.02	0.7	0.6	5	3	Invention
36	3	11	0.15				0.2	0.02				0.7	0.6	5	3	Invention
37	3	11	0.15				0.2		0.02			0.7	0.6	5	3	Invention
38	3	11	0.15				0.2			0.02		0.7	0.6	5	3	Invention
39	3	11	0.15				0.2				0.02	0.7	0.6	5	3	Invention
40	3	11	0.15					0.02	0.02			0.7	0.6	5	3	Invention
41	3	11	0.15					0.02		0.02		0.7	0.6	5	3	Invention
42	3	11	0.15					0.02			0.02	0.7	0.6	5	3	Invention
43	3	11	0.15						0.02	0.02		0.7	0.6	5	3	Invention
44	3	11	0.15						0.02		0.02	0.7	0.6	5	3	Invention
45	3	11	0.15							0.02	0.02	0.7	0.6	5	3	Invention
46	3	11	0.15	0.02	0.02			0.02				0.7	0.6	5	3	Invention
47	3	11	0.15					0.02	0.02		0.02	0.7	0.6	5	3	Invention
48	3	11	0.15		0.02		0.2			0.02		0.7	0.6	5	3	Invention
49	3	11	0.15	0.02		0.02			0.02			0.7	0.6	5	3	Invention
50	3	11	0.15	0.02	0.02	0.02	0.2	0.02	0.02	0.02	0.02	0.7	0.6	5	3	Invention
51	4	8	0.25			0.02	0.2				0.02	0.7	0.6	5	3	Invention
52	5	10	0.3	0.02			0.2			0.02		0.7	0.6	5	3	Invention
53	6	4	0.12		0.02				0.02		0.02	0.7	0.6	4	3	Invention
54	5	15	1.5			0.02		0.02		0.02		0.7	0.6	4	3	Invention
55	1	2	0.06		0.02			0.02	0.02			0.7	0.6	4	3	Invention
56	3	11	0.15									0.4	0.4	3	3	Comparative
57	0	0.2	0									0.7	0.6	1	3	Comparative
58	3	20	0.6					0.02				0.7	0.6	3	3	Comparative
59	0.1	5	0									0.7	0.6	2	3	Comparative
60	3	6	0.005									0.7	0.6	3	3	Comparative
61	3	11	0.15			0.0002						0.7	0.6	4	3	Invention
62	3	11	0.15					0.003				0.7	0.6	4	3	Invention
63	3	11	0.15							0.0003		0.7	0.6	4	3	Invention
64	3	11	0.15			0.0002		0.003				0.7	0.6	4	3	Invention
65	3	11	0.15			0.0002				0.0003		0.7	0.6	4	3	Invention
66	3	11	0.15					0.003		0.0003		0.7	0.6	4	3	Invention

Example 3

Firstly, cold-rolled steel sheets 0.8 mm in thickness were prepared, and subjected to hot dip plating for three seconds at 400 to 600°C in a Zn alloy plating bath wherein the amounts of Mg, Al, Si and other added elements were changed and to N_2 wiping for adjusting the plated amount to 70 g/m^2. The chemical compositions of the plated layers of the plated steel sheets thus produced are shown in Tables 4 to 6. Further, the results of observing the metallographic structures of the plated layers on the cross sections of the plated steel sheets with SEM are also shown in Tables 4 to 6.

The plated steel sheets thus produced were cut into the size of 200 mm x 200 mm, stretched by 35 mm by using a punch 100 mm in diameter with a spherical head, and

thereafter subjected to chemical conversion treatment, painting and the evaluation of corrosion resistance. The phosphate of 2 g/m^2 was applied as the chemical conversion treatment and the urethane group powder coating of 70 μm was applied as the painting.

Further, the painted steel sheets thus produced were scratched, to reach the substrate steel, with a utility knife and then subjected to SST for 500 hours. The evaluation was made by applying tape exfoliation test to the scratches after corrosion test and scoring in accordance with the following criterion based on the length of the exfoliation of a painted film. The marks 3 to 5 were judged to be acceptable.

5: less than 5 mm

4: 5 mm or more to less than 10 mm

3: 10 mm or more to less than 20 mm

2: 20 mm or more to less than 30 mm

1: 30 mm or more

The results of the evaluations are shown in Tables 4 to 6.

In the cases of Nos. 97, 98, 104, 106 and 109, the contents of Mg, Al, Si, Ca, Be, Ti, Cu, Ni, Co, Cr, Mn and Mg_2Si in the plated layers were outside the ranges stipulated in the present invention and resultantly the post-painting corrosion resistance was unacceptable. All the other cases showed good post-painting corrosion resistance and the cases where Mg_2Si was contained in the plated layers showed particularly good corrosion resistance.

Table 4

No.	Hot dip galvanized layer composition (mass%)											Si phase	Mg_2Si phase	Ternary eutectic	Al phase	Zn phase	$MgZn_2$ phase	Corrosion resistance	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn								
1	1	2	0.06	0.05								○		○		○		4	Invention examples
2	1	19	0.6	0.05								○		○	○			4	
3	3	5	0.15	0.05									○	○	○	○		5	
4	4	8	0.25	0.05									○	○	○	○	○	5	
5	5	10	0.3	0.05									○	○	○	○	○	5	
6	5	15	0.45	0.05									○	○	○		○	5	
7	5	15	1.5	0.05									○	○	○		○	5	
8	6	2	0.06	0.05								○		○		○	○	4	
9	6	4	0.12	0.05									○	○		○	○	5	
10	10	2	0.06	0.05								○		○		○	○	4	
11	10	10	0.3	0.05									○	○	○		○	5	
12	3	6	0.1	0.05									○	○	○	○		5	
13	1	2	0.06		0.03							○		○		○		4	
14	1	19	0.6		0.03							○		○	○			4	
15	3	5	0.15		0.03								○	○	○	○		5	
16	4	8	0.25		0.03								○	○	○	○	○	5	
17	5	10	0.3		0.03								○	○	○	○	○	5	
18	5	15	0.45		0.03								○	○	○		○	5	
19	5	15	1.5		0.03								○	○	○		○	5	
20	6	2	0.06		0.03							○		○		○	○	4	
21	6	4	0.12		0.03								○	○		○	○	5	
22	10	2	0.06		0.03							○		○		○	○	4	
23	10	10	0.3		0.03								○	○	○		○	5	
24	3	6	0.1		0.03								○	○	○	○		5	
25	1	2	0.06			0.03						○		○		○		4	
26	1	19	0.6			0.03						○		○	○			4	
27	3	5	0.15			0.03							○	○	○	○		5	
28	4	8	0.25			0.03							○	○	○	○	○	5	
29	5	10	0.3			0.03							○	○	○	○	○	5	
30	5	15	0.45			0.03							○	○	○		○	5	
31	5	15	1.5			0.03							○	○	○		○	5	
32	6	2	0.06			0.03						○		○		○	○	4	
33	6	4	0.12			0.03							○	○		○	○	5	
34	10	2	0.06			0.03						○		○		○	○	4	
35	10	10	0.3			0.03							○	○	○		○	5	
36	3	6	0.1			0.03							○	○	○	○		5	
37	1	2	0.06				0.31					○		○		○		4	
38	1	19	0.6				0.31					○		○	○			4	
39	3	5	0.15				0.31						○	○	○	○		5	
40	4	8	0.25				0.31						○	○	○	○	○	5	
41	5	10	0.3				0.31						○	○	○	○	○	5	
42	5	15	0.45				0.31						○	○	○		○	5	
43	5	15	1.5				0.31						○	○	○		○	5	
44	6	2	0.06				0.31					○		○		○	○	4	
45	6	4	0.12				0.31						○	○		○	○	5	
46	10	2	0.06				0.31					○		○		○	○	4	
47	10	10	0.3				0.31						○	○	○		○	5	
48	3	6	0.1				0.31						○	○	○	○		5	
49	1	2	0.06					0.03				○		○		○		4	
50	1	19	0.6					0.03				○		○	○			4	

Table 5

No.	Hot dip galvanized layer composition (mass%)											Si phase	Mg_2Si phase	Ternary eutectic	Al phase	Zn phase	$MgZn_2$ phase	Corrosion resistance	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn								
51	3	5	0.15					0.03					○	○	○	○		5	Invention
52	4	8	0.25					0.03					○	○	○	○	○	5	Invention
53	5	10	0.3					0.03					○	○	○	○	○	5	Invention
54	5	15	0.45					0.03					○	○	○		○	5	Invention
55	5	15	1.5					0.03					○	○	○		○	5	Invention
56	6	2	0.06					0.03				○		○		○	○	4	Invention
57	6	4	0.12					0.03					○	○		○	○	5	Invention
58	10	2	0.06					0.03				○		○		○	○	4	Invention
59	10	10	0.3					0.03					○	○	○		○	5	Invention
60	3	6	0.1					0.03					○	○	○	○		5	Invention
61	1	2	0.06						0.04			○		○		○		4	Invention
62	1	19	0.6						0.04			○		○	○			4	Invention
63	3	5	0.15						0.04				○	○	○	○		5	Invention
64	4	8	0.25						0.04				○	○	○	○	○	5	Invention
65	5	10	0.3						0.04				○	○	○	○	○	5	Invention
66	5	15	0.45						0.04				○	○	○		○	5	Invention
67	5	15	1.5						0.04				○	○	○		○	5	Invention
68	6	2	0.06						0.04			○		○		○	○	4	Invention
69	6	4	0.12						0.04				○	○		○	○	5	Invention
70	10	2	0.06						0.04			○		○		○	○	4	Invention
71	10	10	0.3						0.04				○	○	○		○	5	Invention
72	3	6	0.1						0.04				○	○	○	○		5	Invention
73	1	2	0.06							0.03		○		○		○		4	Invention
74	1	19	0.6							0.03		○		○	○			4	Invention
75	3	5	0.15							0.03			○	○	○	○		5	Invention
76	4	8	0.25							0.03			○	○	○	○	○	5	Invention
77	5	10	0.3							0.03			○	○	○	○	○	5	Invention
78	5	15	0.45							0.03			○	○	○		○	5	Invention
79	5	15	1.5							0.03			○	○	○		○	5	Invention
80	6	2	0.06							0.03		○		○		○	○	4	Invention
81	6	4	0.12							0.03			○	○		○	○	5	Invention
82	10	2	0.06							0.03		○		○		○	○	4	Invention
83	10	10	0.3							0.03			○	○	○		○	5	Invention
84	3	6	0.1							0.03			○	○	○	○		5	Invention
85	1	2	0.06								0.03	○		○		○		4	Invention
86	1	19	0.6								0.03	○		○	○			4	Invention
87	3	5	0.15								0.03		○	○	○	○		5	Invention
88	4	8	0.25								0.03		○	○	○	○	○	5	Invention
89	5	10	0.3								0.03		○	○	○	○	○	5	Invention
90	5	15	0.45								0.03		○	○	○		○	5	Invention
91	5	15	1.5								0.03		○	○	○		○	5	Invention
92	6	2	0.06								0.03	○		○		○	○	4	Invention
93	6	4	0.12								0.03		○	○		○	○	5	Invention
94	10	2	0.06								0.03	○		○		○	○	4	Invention
95	10	10	0.3								0.03		○	○	○		○	5	Invention
96	3	6	0.1								0.03		○	○	○	○		5	Invention
97	1	2	0.06									○		○		○		2	Comparative
98	1	19	0.6									○		○	○			2	Comparative
99	3	5	0.15										○	○	○	○		3	Invention
100	4	8	0.25										○	○	○	○	○	3	Invention

Table 6

No.	Hot dip galvanized layer composition (mass%)											Si phase	Mg_2Si phase	Ternary eutectic	Al phase	Zn phase	$MgZn_2$ phase	Corrosion resistance	Remarks
	Mg	Al	Si	Ca	Be	Ti	Cu	Ni	Co	Cr	Mn								
101	5	10	0.3										○	○	○	○	○	3	Invention
102	5	15	0.45										○	○	○		○	3	Invention
103	5	15	1.5										○	○	○		○	3	Invention
104	6	2	0.06									○		○		○	○	2	Comparative
105	6	4	0.12										○	○		○	○	3	Invention
106	10	2	0.06									○		○		○	○	2	Comparative
107	10	10	0.3										○	○	○		○	3	Invention
108	3	6	0.1										○	○	○	○		3	Invention
109	5	10												○	○	○	○	2	Comparative
110	3	6	0.005										○	○	○	○		3	Invention
111	1	2	0.06			0.0002						○		○		○		4	Invention
112	1	19	0.6			0.0002						○		○	○			4	Invention
113	3	5	0.15			0.0002							○	○	○	○		5	Invention
114	4	8	0.25			0.0002							○	○	○	○	○	5	Invention
115	5	10	0.3			0.0002							○	○	○	○	○	5	Invention
116	5	15	0.45			0.0002							○	○	○		○	5	Invention
117	5	15	1.5			0.0002							○	○	○		○	5	Invention
118	6	2	0.06			0.0002						○		○		○	○	4	Invention
119	6	4	0.12			0.0002							○	○		○	○	5	Invention
120	10	2	0.06			0.0002						○		○		○	○	4	Invention
121	10	10	0.3			0.0002							○	○	○		○	5	Invention
122	3	6	0.1			0.0002							○	○	○	○		5	Invention
123	1	2	0.06					0.003				○		○		○		4	Invention
124	1	19	0.6					0.003				○		○	○			4	Invention
125	3	5	0.15					0.003					○	○	○	○		5	Invention
126	4	8	0.25					0.003					○	○	○	○	○	5	Invention
127	5	10	0.3					0.003					○	○	○	○	○	5	Invention
128	5	15	0.45					0.003					○	○	○		○	5	Invention
129	5	15	1.5					0.003					○	○	○		○	5	Invention
130	6	2	0.06					0.003				○		○		○	○	4	Invention
131	6	4	0.12					0.003					○	○		○	○	5	Invention
132	10	2	0.06					0.003				○		○		○	○	4	Invention
133	10	10	0.3					0.003					○	○	○		○	5	Invention
134	3	6	0.1					0.003					○	○	○	○		5	Invention
135	1	2	0.06							0.003		○		○		○		4	Invention
136	1	19	0.6							0.003		○		○	○			4	Invention
137	3	5	0.15							0.003			○	○	○	○		5	Invention
138	4	8	0.25							0.003			○	○	○	○	○	5	Invention
139	5	10	0.3							0.003			○	○	○	○	○	5	Invention
140	5	15	0.45							0.003			○	○	○		○	5	Invention
141	5	15	1.5							0.003			○	○	○		○	5	Invention
142	6	2	0.06							0.003		○		○		○	○	4	Invention
143	6	4	0.12							0.003			○	○		○	○	5	Invention
144	10	2	0.06							0.003		○		○		○	○	4	Invention
145	10	10	0.3							0.003			○	○	○		○	5	Invention
146	3	6	0.1							0.003			○	○	○	○		5	Invention

Industrial Applicability

The present invention makes it possible to produce a plated steel sheet which is excellent in corrosion resistance and paint coat image clarity when it is used after being processed and painted.